

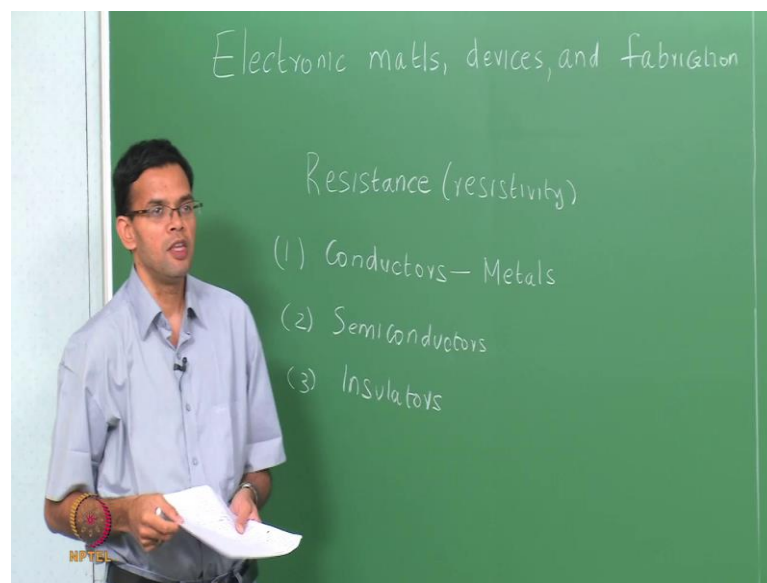
**Electronic Materials, Devices and Fabrication**  
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**Lecture Number - 01**  
**Metals, Semiconductors and Insulators**

Welcome to the first lecture of this course electronic materials devices and fabrication. In this course, we will look at semiconductor materials we will study the properties mostly the electronic properties we will then use these semiconductor materials to form devices. So, these devices could be made from 2 semiconductors, they could be made from a semiconductor and a metal or even a semiconductor, insulator and a metal. We will also looked at devices for some optical applications like say LEDs and solar cells.

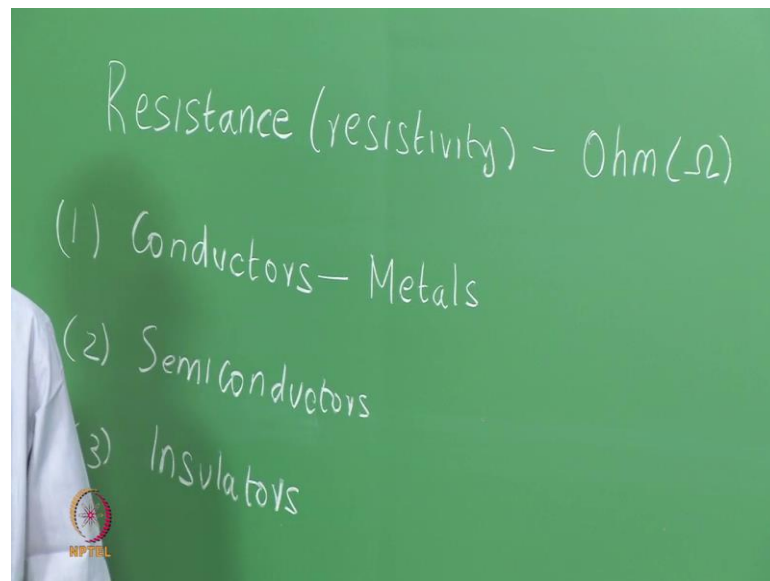
Finally, we will look at the current micro fabrication industry where we will form integrated circuits made of these devices from semiconductors. Towards the end of the course, we will also look at some alternate fabrication techniques where we used a bottom of approach to fabricate devices rather than the top down approach there is currently following. When we think of electronic materials, the first property that comes to mind is resistance.

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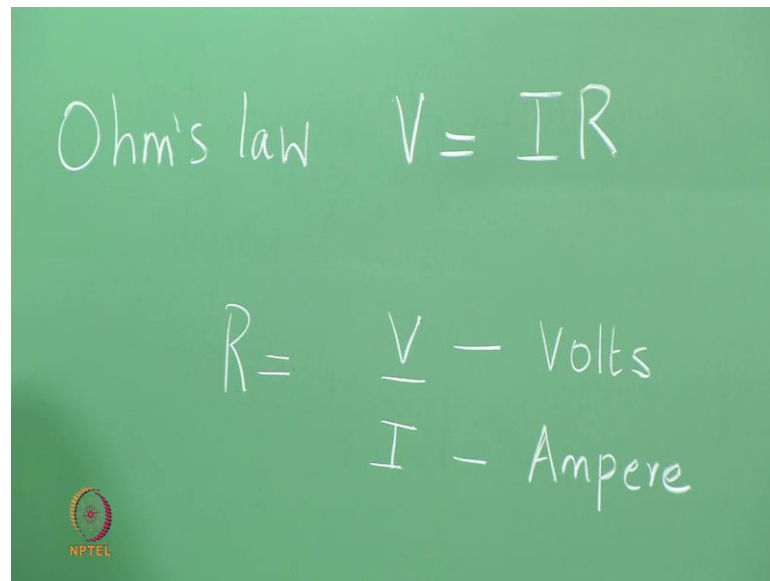
Resistance or resistivity if you will can be used in order to separate materials into 3 categories: the first one is conductors then, you have semiconductors and then finally, you have insulators. Since will be mostly dealing with metals as conductors I will also write them as just metals, when we think of resistance the unit of resistance is ohm and the symbol is omega.

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Resistance is related to both the voltage and the current by what is known as Ohm's Law.

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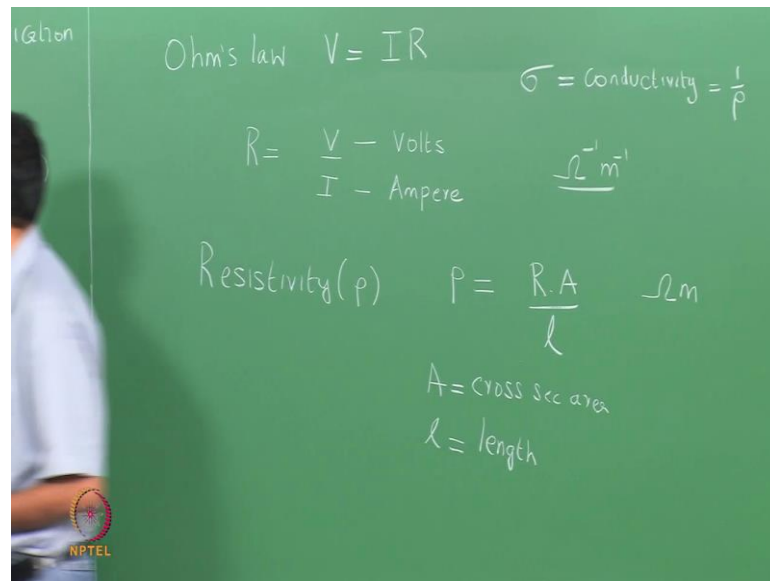
Ohm's law  $V = IR$

$R = \frac{V}{I}$  - Volts  
I - Ampere

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Ohm's Law states the voltage is nothing, but the current times the resistance and other way of writing it is resistance is voltage over current. A unit of a voltage is volts a unit of current is Ampere. Now, resistance depends upon the dimensions of the sample. So, if we have thinner material or if we have a wire with a smaller diameter then the resistance is higher. So, we need to think of a parameter that does not depend a part on the dimensions of the sample.

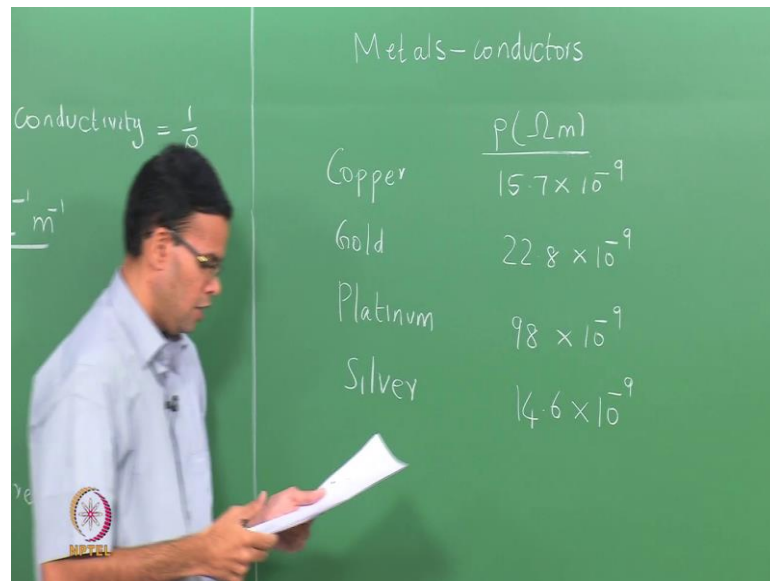
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And this parameter is called Resistivity; Resistivity is typically given as  $\rho$  and it is related to the resistance by, where R is the resistance; A is the cross sectional area and l is the length of the sample. The unit of resistivity is ohm meter you can also have ohm centimeter, 1 over the resistivity is called Conductivity. The unit of conductivity is nothing, but ohm inverse meter and meter inverse.

So, we have introduced 2 concepts: one is the Resistivity, the other is the Conductivity. We also said we have 3 types of materials: conductors, semiconductors and insulators and the difference between them is because of the difference in the resistivity value. So, let us look at some typical values for resistivity for all these 3 types.

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Let us, start with metals or conductors some typical examples of metals: Copper, Gold, Platinum, Silver were are some of the typical resistivities. So, rho unit is ohm meter in the case of Copper 15.7 times 10 to the minus 9; for gold 22.8 10 to the minus 9 is common for all 4. Platinum is slightly higher its 98, Silver is actually a better conductor then copper, but silver is also expensive.

So, when we look at metals we have conductivity or we have resistivity of around 10 to the minus 9 ohm meters. let us, next look at semiconductors.

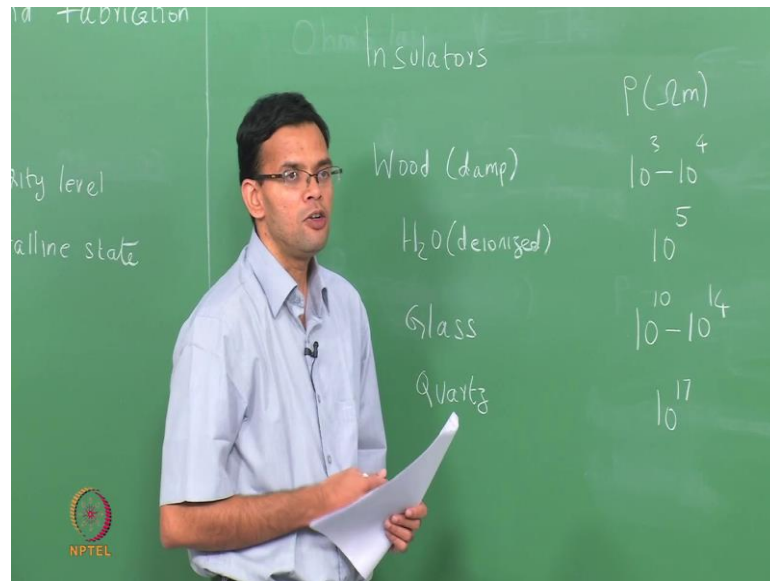
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	$\rho (\Omega m)$	
Ge	$10^{-3}$	Impurity level
Si	$0.1 - 10^3$	crystalline state
ZnO	$10^{-2} - 10^{-4}$	
GaAs	$10^{-6} - 10^{-2}$	

Some examples of semiconductors, Germanium, Silicon, Zinc Oxide, Gallium Arsenide, some of the typical values of resistivity: Silicon is around 0.1 to  $10^3$ ; Zinc Oxide is  $10^{-2}$  to  $10^{-4}$  is lower; Gallium arsenide  $10^{-6}$  to  $10^{-2}$ . In all of these cases have given range of values the actual resistivity, all the conductivity depends upon the impurity level and also the crystal in state, whether you have a single crystal or a polycrystal.

So, these are some of the values for resistivity in the case of semiconductors. What about insulators?

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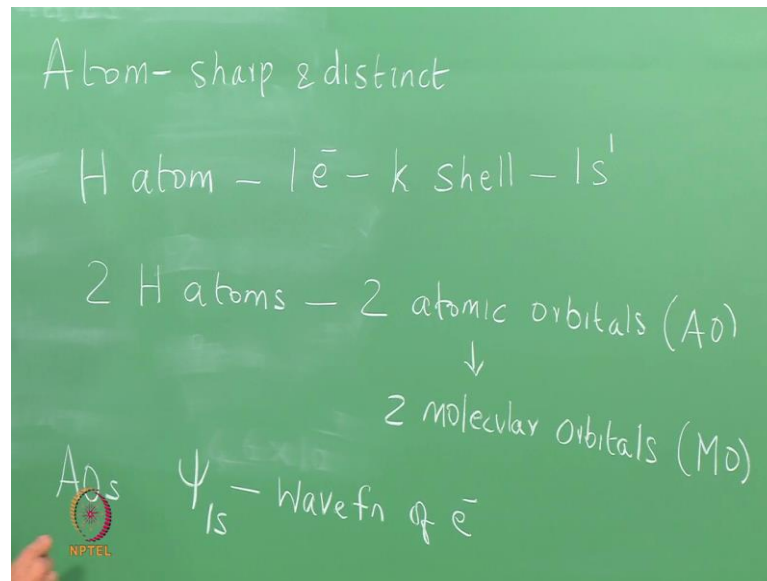


Examples of some typical insulators we could say, Wood, Water deionized water. So, they know dissolved salts, Glass and Quartz these are some typical values. So,  $10$  to the  $5$ ; the clays of glass resistivities around  $10$  to the  $10$  to  $10$  to the  $14$  depending upon if you have some doping agents in glass or not for some impurities in case of quartz its even higher.

So, what we essentially see is a wide range of resistivity depending upon, whether you are the metal or you have a semiconductor or you have an insulator. So, the question is how to understand this difference in these values? In order to do that, we need to look at the band gap of the material and how the band gap evolves? All focus will be mainly on metals and semiconductors.

But what about concept we develop we can equally apply them to insulators. So, let us go ahead and look at how band gap evolves starting with a metal; when you have an individual atom the energy levels are usually sharp and distinct.

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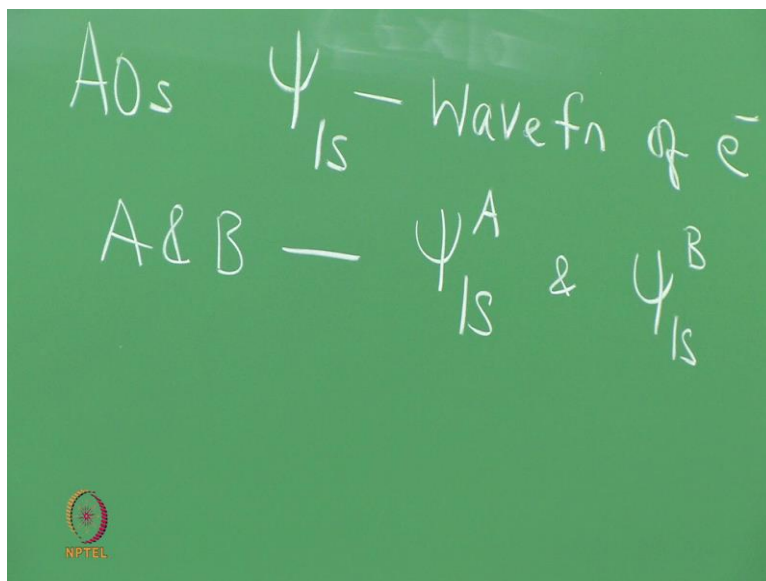


The question really is, what happens when all these items come together to form a solid. So, let us start with the simplest atom that we know that is the Hydrogen atom. Hydrogen atom has 1 electron and has 1 proton in Nucleus; the 1 electron is in the k shell and the atomic configuration for Hydrogen is  $1s^1$ . What happens when we have 2 Hydrogen atoms come together? When we have 2 Hydrogen atoms, you have 2  $1s$  atomic orbitals that come together these interact and give you 2 molecular orbitals.

So, 2 Hydrogen atoms have 2 atomic orbitals which give you 2 molecular orbitals. For sake of gravity I will call atomic orbitals as AO and molecular orbitals as MO. Let us, denote these atomic orbitals by the symbol  $\psi_{1s}$ ;  $1s$  refers to the fact that you will have the electron in the 1st shell. In quantum mechanics  $\psi$  represents the wave function of the electron.

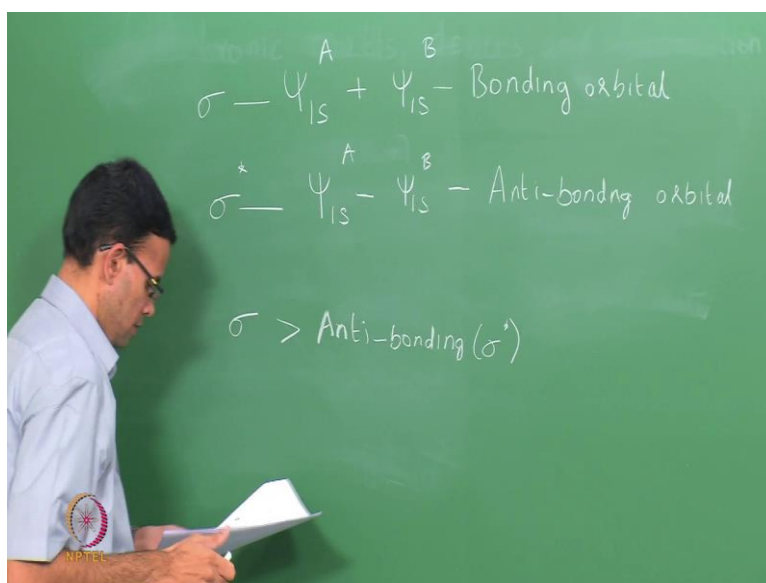


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If you have 2 Hydrogen atoms A and B; you have 2 atomic orbitals let's call them  $\psi_{1s}^A$  and  $\psi_{1s}^B$ . Now, in order to form molecular orbitals these 2 wave functions  $\psi_{1s}^A$  and  $\psi_{1s}^B$  have to be put together and there are 2 ways of doing it.

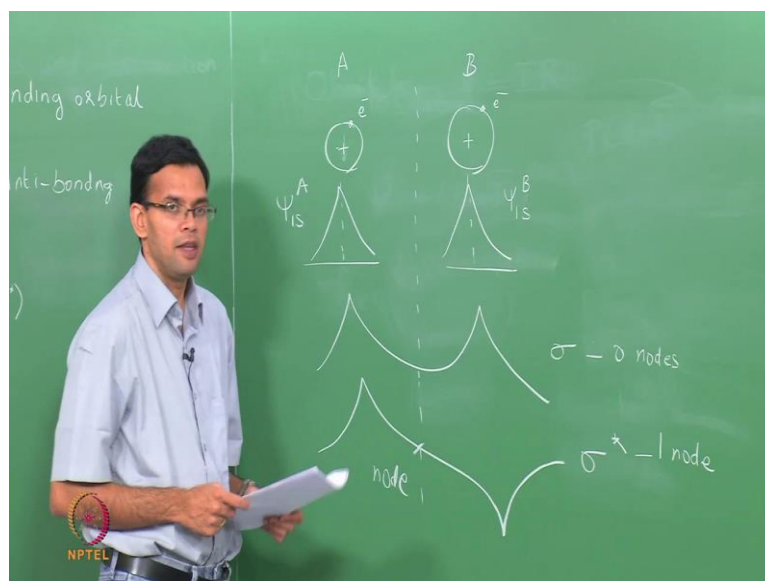
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We could add both of them this is called a Bonding orbital and it is denoted by  $\sigma$  we

can subtract them and this is called the Anti-Bonding orbital. In terms of energy the Bonding orbitals sigma has a higher energy than the Anti-bonding orbital and I am going to denote this as sigma star. So, I will call this sigma star we can also depict this pictorially.

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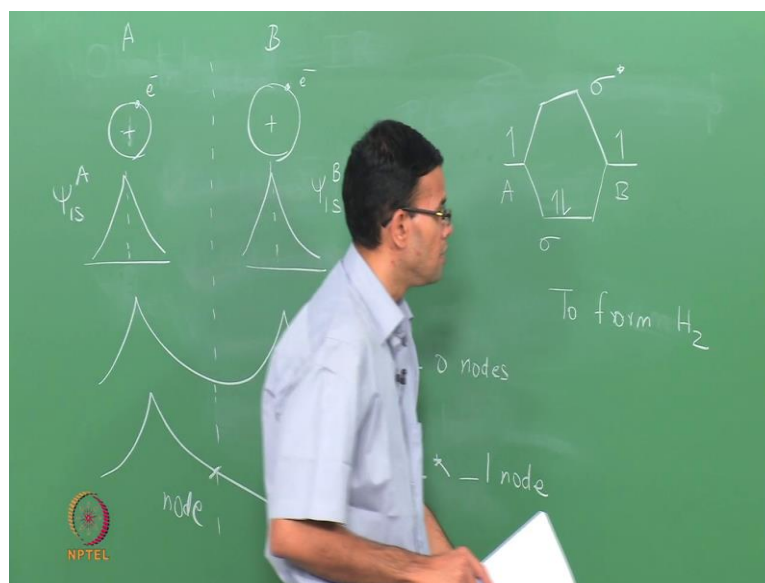
So, let us take 2 Hydrogen atoms so at the center you have the nucleus and outside you have the electron A and B each of them has an atomic orbital. So, on atomic way function so, this is  $\psi_{1s}$  of A this is the atomic orbital for A;  $\psi_{1s}$  to B in both of these cases I have chosen an exponential function for the atomic orbitals. There is a way of showing that it is actually an exponential function, but we won't go into it.

As far as wave function concerned we have an orbital that exponentially goes decreasing away from the nucleus and we will still keep it at that. So, now we had 2 atomic orbitals we can either add them or subtract them. If you add them the result and wave function look something like this. So, you have a minimum between the 2 atoms and you have a maximum at the 2 nuclei.

So, this is your Bonding orbital will call it sigma, we can also subtract them which case this is the Anti-bonding orbital that is sigma star. You look at it, sigma does not go to 0

at all it goes to minimum; between the 2 atoms and the other hands stigma star goes to a 0 between the 2 atoms and this is called a node. So, the sigma has 0 nodes and the sigma star has 1 node. So, we say that the sigma has a lower energy than sigma star write the Bonding orbital is most stable to the Anti Bonding.

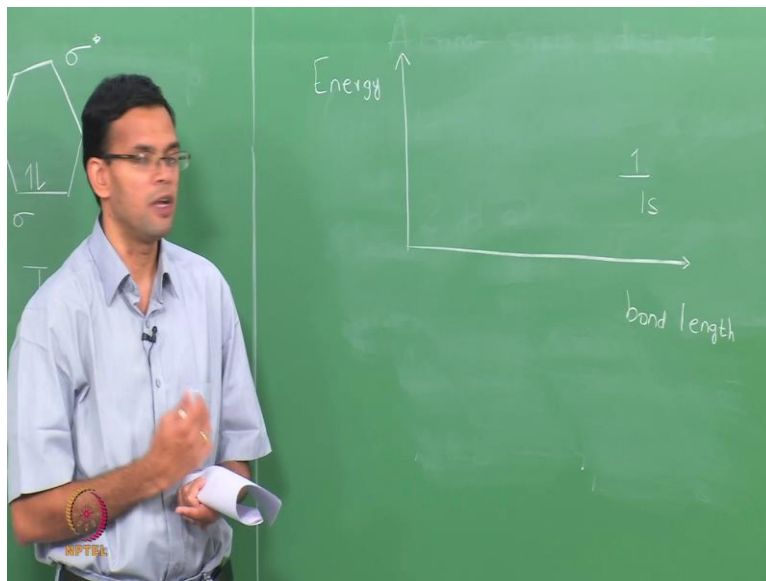
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And another way to represent this compactly is to consider you 2 Atomic orbitals A and B each has 1 electron and these 2 much they form both a Bonding and a Anti-bonding orbital. So, a Bonding orbital has a lower energy that is your sigma; Anti-bonding orbital has a higher energy that is sigma star each orbital can take to electrons of opposite spin.

So, both electrons go to the sigma first, when you form a Hydrogen molecule from 2 Hydrogen atoms the overall energy of the system is lower. Such favorable to form H<sub>2</sub> and 2 Hydrogen atoms come together. We can also show this diagram by means, of an energy verses bond length diagram.

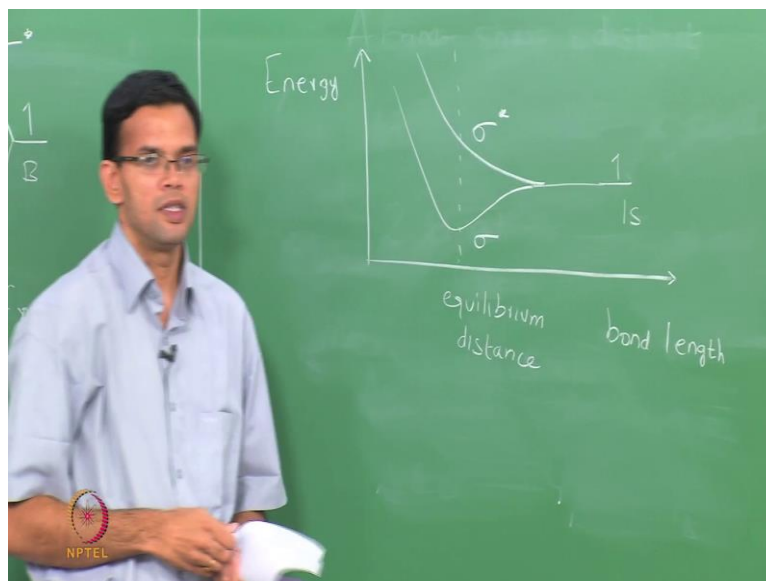
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And in that particular plot, you have energy on the y axis and you will have Bond length on the x axis so, energy this is bond length. Then, the 2 Hydrogen atoms are far apart typically we said that the Hydrogen atoms are infinity then, what we have the simply the atomic orbitals. So, I will show them here choose the 1s orbital in a has 1 electron then you start to bring your Hydrogen atoms together.

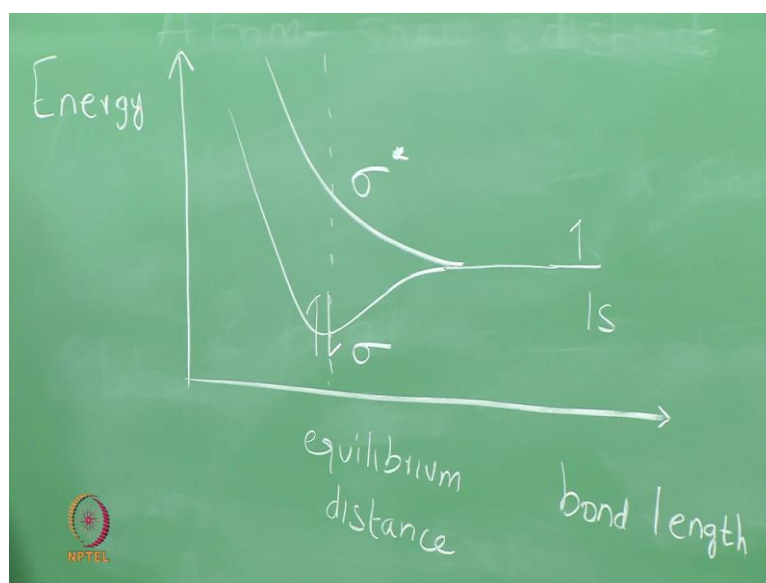
So, as a start to come together they will see the effect of each other; ultimately the atomic orbitals will mix and give you your molecular orbitals sigma and sigma star.

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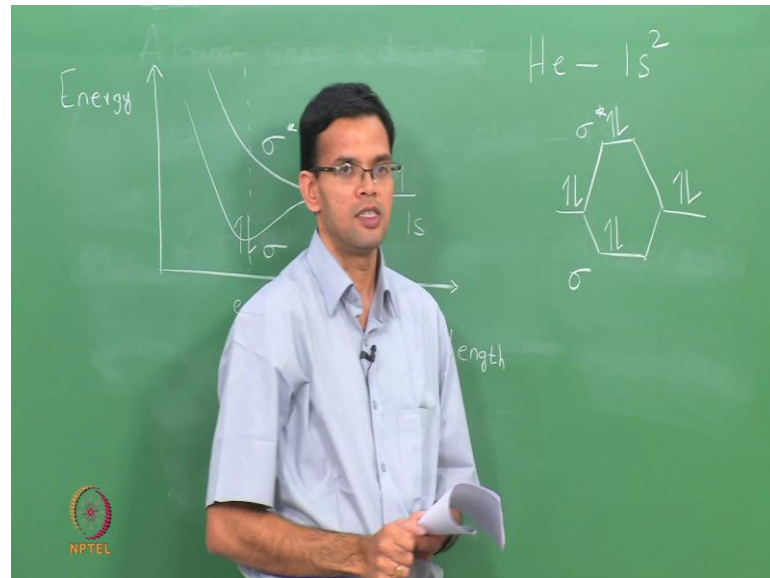
So, for this we will have some equilibrium distance. So, let me call this equilibrium distance choose the equilibrium distance for the 2 Hydrogen atoms in the molecule. So, you now have the atoms come together they form 2 molecular orbitals: 1 is sigma, the other is sigma star. So, sigma as a lower energy is the Bonding, sigma star has a higher energy that is Anti-bonding.

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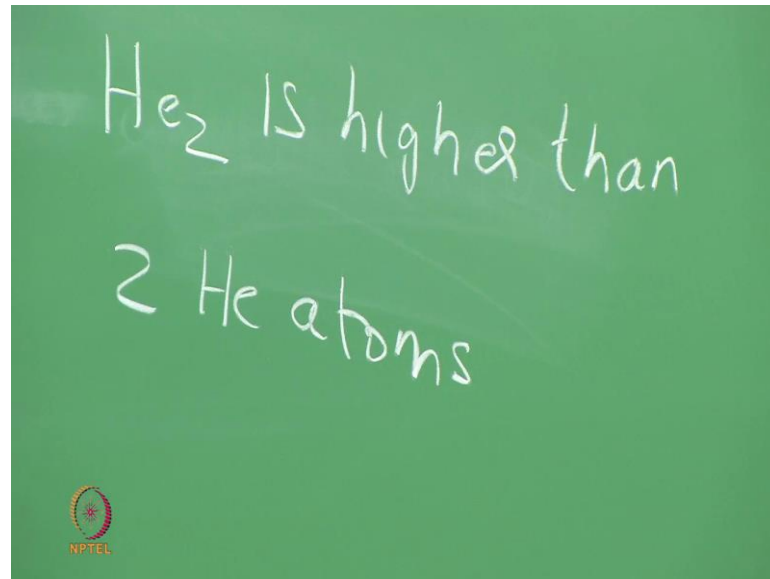
And both electrons go into sigma so, this is the picture as far as Hydrogen is concerned. Right we can use to saying diagram to explain why Helium to will not form.

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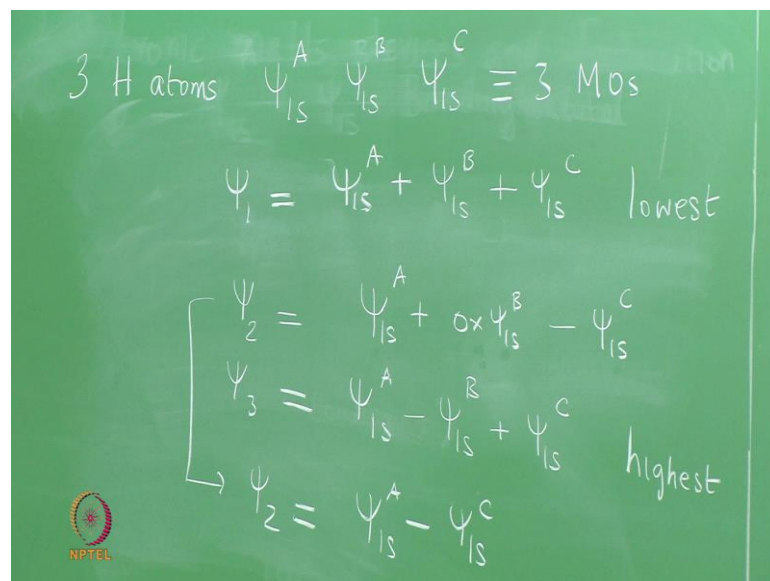
The case of Helium is a noble gas it has 2 electrons in the 1s shell, if 2 Helium atoms come together. So, you have 2 electrons here, you have 2 electrons here once again both the 1s you can think of mixing and forming a Bonding and Anti-bonding. So this is your sigma, this is your sigma star. So, now we have a total of 4 electrons 2 electrons will go into sigma, but 2 electrons also go into the Anti-bonding that is sigma star.

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So, the overall energy of Helium 2 is higher than just 2 Helium atoms. So, that is why you will not have Helium 2 this picture is good enough as long we have 2 atoms. Now, what if I had 3 hydrogen atoms let us, look at that.

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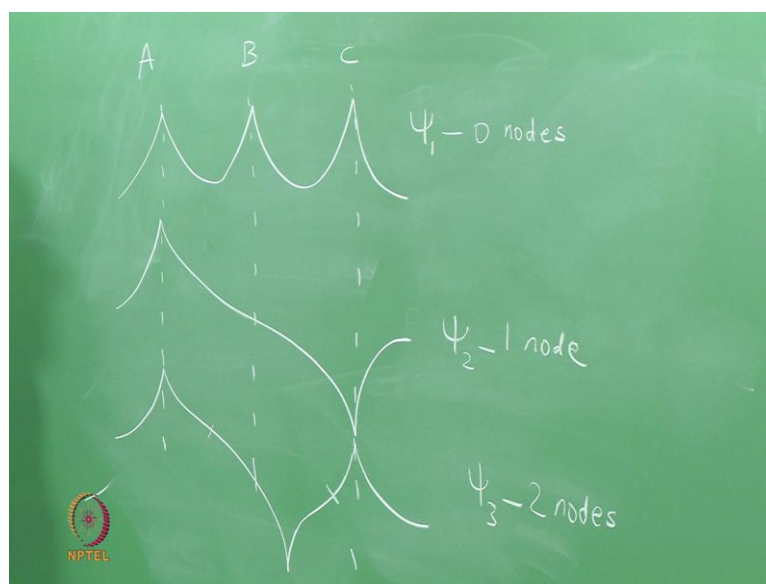


So, let us say we have 3 Hydrogen atoms a, b and c. So, your atomic orbitals are psi 1s

A,  $\psi_{1s} B$ ;  $\psi_{1s} C$  when we have 2 atoms we said they form 2 orbitals 2 molecular orbitals. Now, we have 3 atoms we have going to get 3 molecular orbitals. There are 3 ways of obtaining these molecular orbitals: the first 1 is to just add all 3 this is the lowest energy.

You can also do 1 subtraction this is the lowest energy, this has the highest energy and then you 1 more in between them. So, in this particular case the contribution from the second Hydrogen atom is neglected because it is time 0. So, all you have is  $\psi_{1s} A$  and minus  $\psi_{1s} C$ . So, let me write just the down  $\psi_2$  is nothing, but  $\psi_{1s} A$  and  $\psi_{1s} C$ . We can depict this pictorially again by taking 3 hydrogen atoms.

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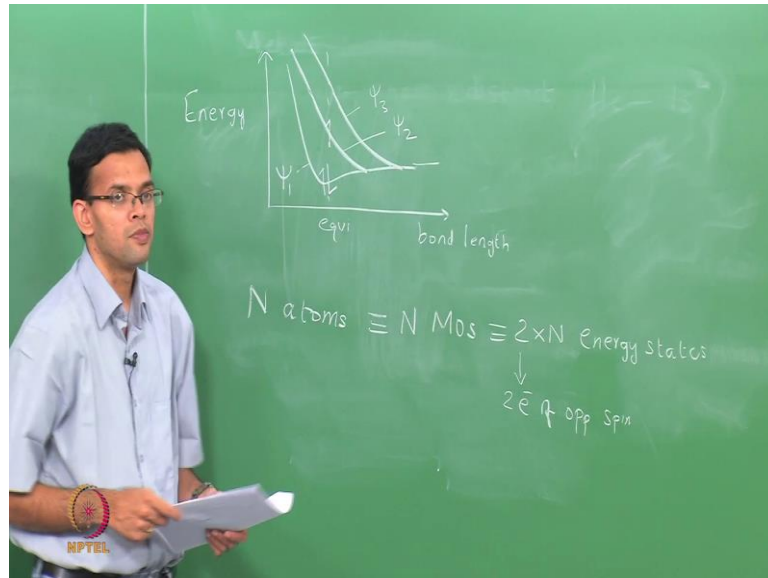
So, in the first case you are adding all 3 orbitals together. So, these are A B and C this is  $\psi_1$  you are adding all 3; this 1 the function does not go to 0 anywhere. So, you have 0 nodes in the case of  $\psi_2$  we said the function goes to 0 at atom B. So, that is why there is only contribution from A and C this is  $\psi_2$  so, it has 1 node. And in the case of  $\psi_3$  we have 2 nodes.

So, this is the lowest energy with 0 nodes when you have 1 node which is the higher energy. Finally,  $\psi_3$  that has the highest energy for this case also we can draw an energy



was its bond length diagram.

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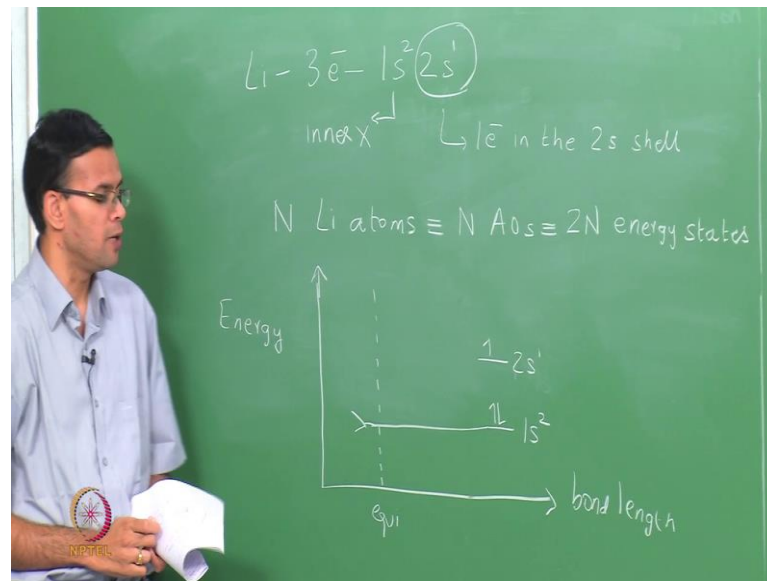


If you do the energy verses bond length for 3 Hydrogen atoms what we have are 3 orbitals psi 1 with the lowest, psi 3 with the highest and then the psi 2 in the middle. Now, we have 3 electrons 2 electrons will go to psi 1, 1 electron will go to psi 2. So, this is what we happened we have 3 Hydrogen atoms. Now if you have 4 Hydrogen atoms, you will have 4 molecular orbitals, you will have 4 lines here, 5 you will have 5 lines here.

So, thus as the number of atoms increases you will have more lines in your energy verses bond length diagram. So, ultimately we can say we have N atoms could be N Hydrogen atoms then, you will have N molecular orbitals each molecular orbital can take 2 electrons of opposite spin. So, 2 times N energy states. And number 2 comes because, you can have 2 electrons of opposite spin.

So, this is the picture you developed using Hydrogen we also showed how Helium will not bond; what if I increase the complexity of bit further and then looked at Lithium.

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We have Lithium has 3 electrons so, the electronic configuration is  $1s^2 2s^1$ ; the  $1s$  shell in Lithium is an inner shell. So, this is an inner shell the inner shell is usually not involved in bonding so, we would ignore the effect of the inner shell. So, what we are interested in is the  $2s^1$  electron right. So, this again has 1 electron in the  $2s$  shell so, this is similar to a Hydrogen atom.

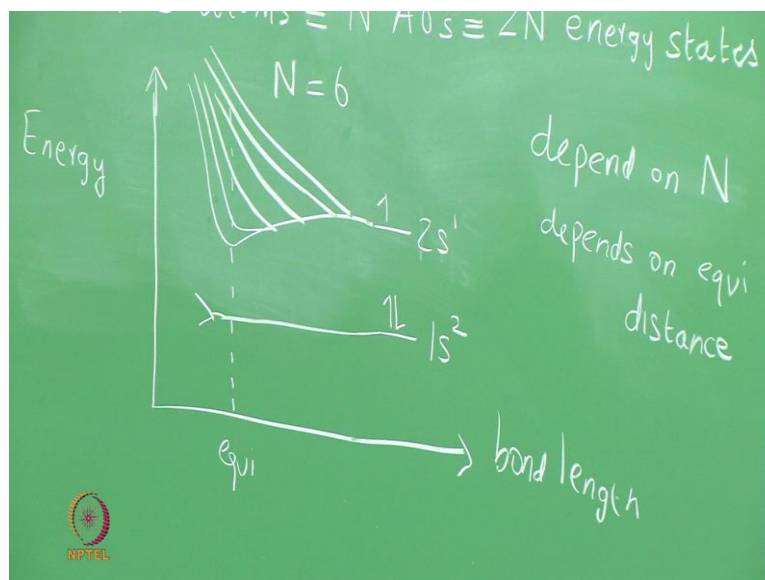
So, we can use the same argument for Lithium as in the case of Hydrogen. So, if we have  $N$  Lithium atoms taking only the  $2s$  electrons into account, you have  $N$  atomic orbitals which will give you  $2N$  energy states. Again  $\sqrt{2}$  because, each energy state or each molecular orbital we can have 2 electrons. Once again, we can draw an energy versus bond length diagram for Lithium.

So, we have energy on the  $y$  axis bond length on  $x$  axis so, energy bond length when you have the equilibrium space and here. This is the equilibrium spacing of the Lithium atoms when they come together to form a solid. So, you will have the  $1s^2$  which is an inner shell has 2 electrons as a said the inner shell does not take part in bonding. So, which remains a straight line does not form a band.

Now, you have the  $2s^1$  if you have  $N$  Lithium atoms the  $2s^1$  of all of those Lithium

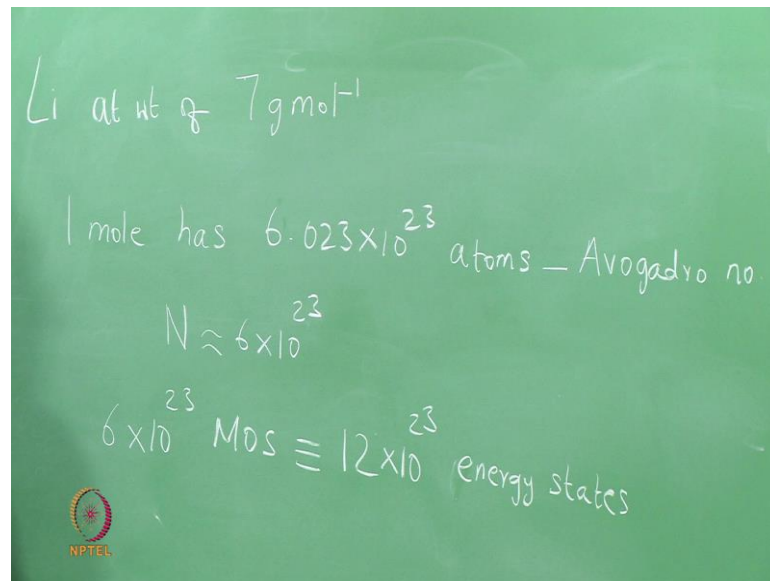
atoms come together to form  $N$  molecular orbitals.

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So, once again we can draw this picture where will have end lines here in this particular case I will draw 1 2 3 6 lines. So, in this particular case  $N$  is 6 the spacing between these lines depend upon  $N$  and it also depends on the equilibrium distance. So, what is a typical value of  $N$ ?  $N$  is usually a very large number.

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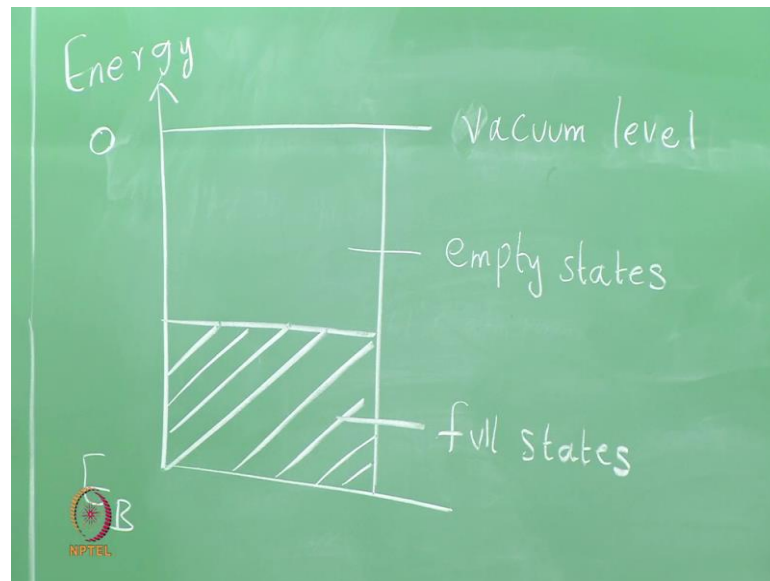


For example, if you take Lithium has an atomic weight of 7 grams per mole right. So, if you have 7 grams of Lithium you have 1 mole and 1 mole has 6.023 times 10 to the 23 atoms. Right this is nothing, but the Avogadro number. So, you have a typical value of N if he had 7 grams of material is approximately 6 times 10 to the 23. So, if we have 6 times to the 23 Lithium atoms coming together to form a solid you have 6 times 10 to the 23 molecular orbitals each of them can take 2 electrons.

So, you have 10 times or 12 times 10 to the 23 energy states and this is a really large number. So, what this means is the spacing between the individual energy states is really small. If you go back to the diagram, the diagram will be draw here and had N equal to 6 and draw 6 lines you have N equal to 23 10 to the 23 you are essentially drawing 10 to the 23 of these lines.

So, what I am trying to say is really large ends these become continues and what we have is an energy band. So, we can redraw the energy band diagram for Lithium taking into fact that you no longer have individual molecular orbitals, which you have an energy band.

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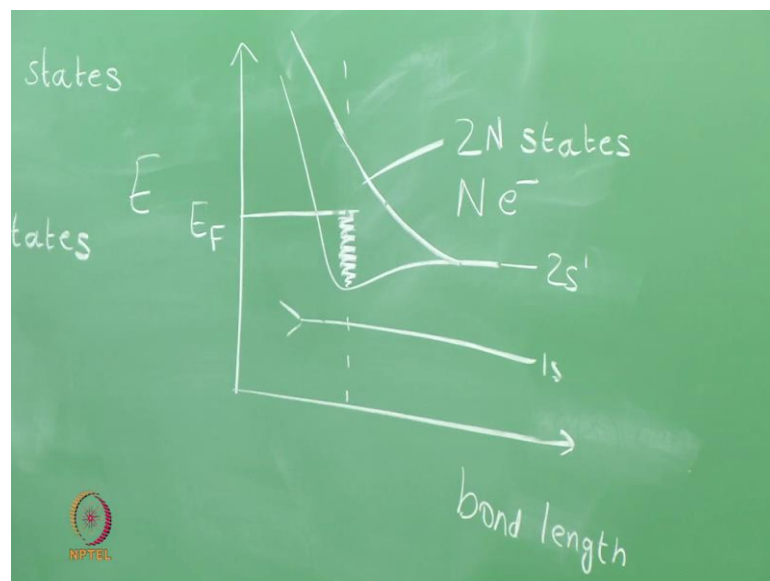
So, in this case the energy is on the y axis we reference an energy level calls 0 which is the Vacuum level. So, let me call this is the Vacuum level and this has a value 0. So, everything can be reference to the vacuum level. So, you have an energy band that is halfful. So, in this case these are all the full states and these are all the empty states. So, how do we arrive the fact that the energy band is halfful, we go back to the energy verses the bond length diagrams.

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Energy versus bond length we have Lithium which is  $2s^1$  you have  $1s$  inner shell, you have  $2s^1$ . So, this is the energy band here and there are a total of  $2$  end states, but each Lithium atom will only contribute  $1$  electron.

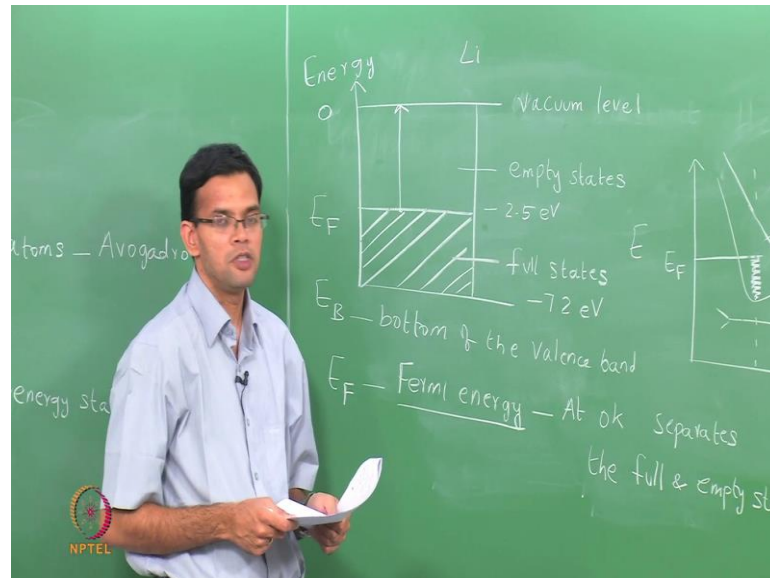
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So, you have only  $2N$  electrons so, hence only half of this band is full. So, we can erase

the top half. So, you have a situation where you have half of the band there is full, half of the band there is empty. This is the same thing I have showed here you have a half a band there is full, you have half a band there is empty.

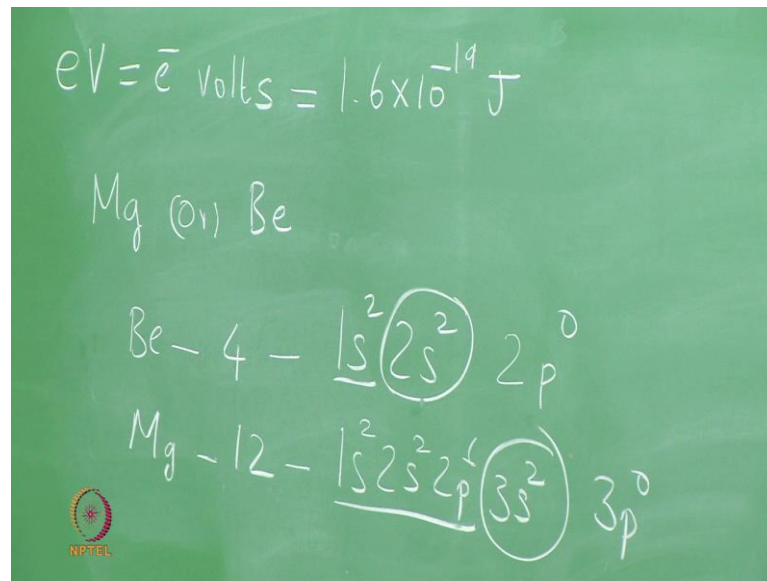
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This energy state that separates the full and the empty regions I have labeled it as a  $E_F$  is called the Fermi Energy. Now, this is a very important term the Fermi Energy at 0 Kelvin separates the full and empty states. So, Fermi Energy separates the full and empty state this is the most often used working definition for Fermi Energy. When we come to semi conductors you will try to modify this definition a little, but as far as dealing with metals we will use this.

So, let us just put some numbers here so, in the case of Lithium this energy is 0; the Fermi energy is at minus 2.5 eV. Which means, you need 2.5 eV of energy in order excite an electron from the Fermi level to the Vacuum level.  $E_B$  is the bottom of the valence band, in the case of Lithium  $E_B$  has a value of minus 7.2 eV. So, the units of energy that I used here eV is called Electron Volts.

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The eV is called electron volts it related to the energy in Jules by the expression 1.6 and extend to the minus 19 Jules. So, 1 eV is approximate is 1.6 times 10 to the minus 19 Jules this is the picture as far as Lithium is concerned. So, in the case of Lithium you have a 2s shell that is halfful. So, you will also have a band that is halfful. What about Magnesium or Beryllium?

So, Beryllium has an atomic number of 4 so, it has an electronic configuration  $1s^2 2s^2$  Magnesium is below Beryllium in the periodic table has an electronic configuration  $1s^2 2s^2 2p^6$  and  $3s^2$ . Once again, for both of these elements these are the inner shell so, you a outer shell is essentially an s2 configuration. This configuration is a same as, in the case of Helium you saw that Helium has  $1s^2$  configuration.

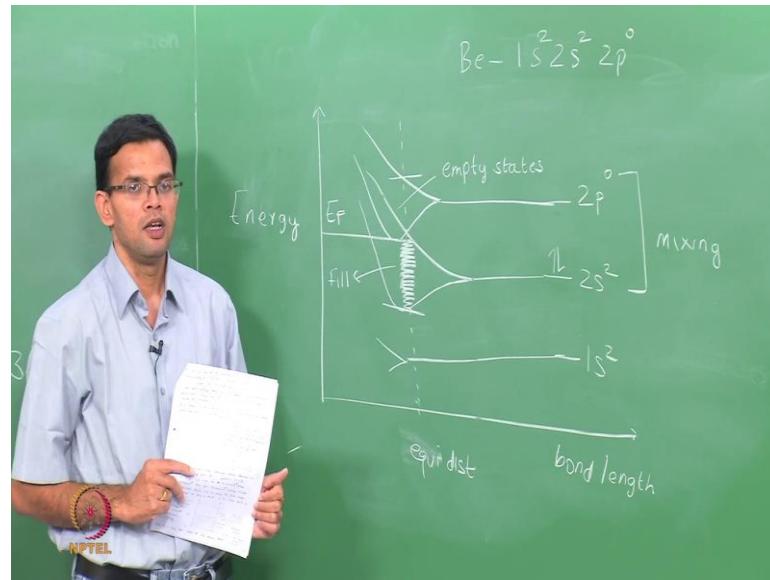
The question is, how will Beryllium or Magnesium form metals or a form a solid? Because, we know they do and Helium does not. The reason is in the case of both Beryllium and Magnesium you also have the pea shells and the pea shells are empty. So, here you have a  $2p^0$  in the case of Magnesium you have a  $3p^0$ . So, what you have when you form a solid is a mixing between the empty  $2p^0$  and the full  $2s^2$ .

In the case of Magnesium you have mixing between the empty  $3p^0$  the full  $3s^2$  and that



is the reason why you have an unfilled state and why these are metals. So, this once again we can show this pictorially using the energy versus the bond distance diagram.

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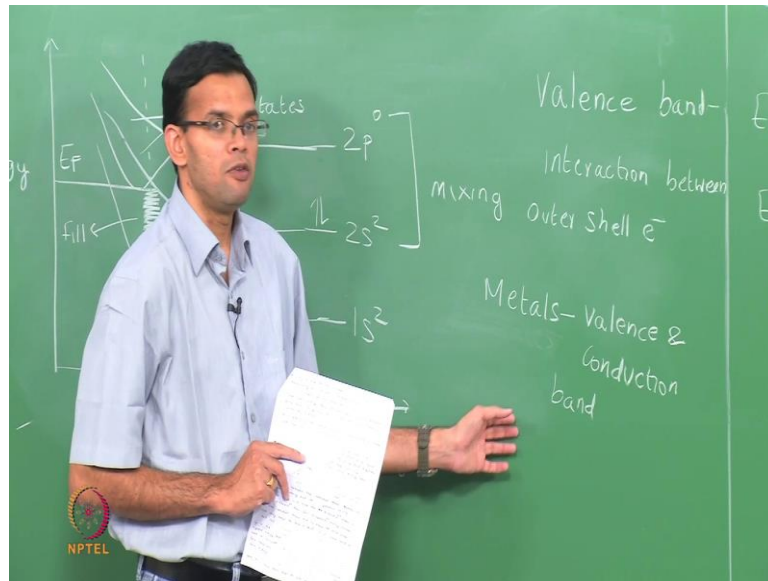


So let us, use the example for Beryllium you have energy on the y axis and then bond length and the x axis and we have some equilibrium distance. The 1s shell is an inner shell, but will not take part in bonding you have a 2s shell that is full and you have a 2p<sup>0</sup> that is empty. So, when draw the bond diagram this is your 2s shell which also have the 2p<sup>0</sup> shell. So, what you have is the mixing of the 2s and the 2p.

So, that this whole thing which a mixture of the 2s and the 2p forms a band then, you can fill in the electrons in this band. So, that these are all the full states these are all the empty states. And the energy separating the full and the empty states is you Fermi energy. So, that is the reason while Beryllium or Magnesium even though have a full 2s<sup>2</sup> electronic configuration are still considered metals.

Because, they have mixing between the s and the p so, that now they have a band there is half full and half empty. This band which is caused by interaction of the electrons on the outer more shell is calling the Valence Band.

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This is caused by the interactions between the outer shell electrons. There is also a conduction band in the case of metals the valence band and the conduction band are both the same. Some case of metals we have both valence in a conduction band and they are both the same. In the case of semiconductors, you will find that the valence and the conduction band are different and there is a gap between them this is what we called the Band gap.

So, in today's class we looked at how metals form so, how you can start with individual atoms and then these atoms come together to form molecular orbitals in the case of metals. We find these molecular orbitals ultimately form a band and these bands are not completely full. There will always some empty states are available and this is why metals are such good conductors,

Because, these electrons which are there in these bands you can acquire energy and go to these empty states. And thus can move freely within the metal and this makes metals very good conductors. In next class we will start to look at semiconductors and you will see how we have a band gap in semiconductors, we will also look at different classifications of semiconductor.